

# Decomposition of Mould Resin in Spent Capacitors by NaOH for the Recovery of Tantalum

Takaaki Wajima

**Abstract**—This research investigated the decomposition of mould resins in tantalum capacitors using sodium hydroxide (NaOH) for the recovery of tantalum. Specifically, NaOH was introduced into a reactor, and heated at the required temperature (350–650 °C) in an electric furnace under nitrogen flow. When the set temperature was attained, the tantalum condenser was introduced into the reactor, and heated at varying times for 5 min to 24 h. Following cooling to room temperature, the capacitor was recovered by filtration after treating with distilled water. The weight of the residue after filtration was determined to calculate the decomposition ratio. The elements in the filtrate were determined by atomic absorption spectroscopy and ion chromatography. The composition of the evolved gases was analyzed by gas chromatography. The decomposition ratios were comparable within the heating temperature range studied and reaction time of 24 h. A large amount of silica was eluted into the filtrate. At  $\geq 600$  °C, collapse of the tantalum components was observed, and the degree of elution of tantalum and chloride into the solution was high. At 530 °C, decomposition occurred rapidly and the decomposition ratio was almost constant after 5 min of reaction. An increase in the amounts of gas produced and halogens in the filtrate occurred within 20 min of reaction. Thus, recovery of the tantalum components from the capacitors was successful upon reaction with NaOH at 530 °C for 5 min owing to the effective decomposition and removal of the mould resin from the capacitor. Furthermore, most of the halogen gases generated from the decomposition of the mould resin could be trapped in NaOH, thereby inhibiting exhaustion of halogen gases. These results indicate that the recovery of tantalum from spent capacitors using NaOH is a feasible approach to recycle rare metals in electric equipments.

**Index Terms**—Tantalum recovery, Decomposition of mould resin, NaOH, Halogen gas.

## I. INTRODUCTION

Rare metals are indispensable resources for the manufacture of various electronic devices, and their demand is increasing. However, the cost and output of rare metals vary owing to the uneven distribution of rare metal resources across the world. Tantalum is one of the rare metals used in capacitors in electronic devices. Tantalum capacitors with high tantalum contents are manufactured in smaller sizes, and display higher performance than other types of capacitors. Tantalum capacitors are used in many products such as personal computers and servers and small-sized home appliances. Owing to the annual increase in demand, a rather

large number of spent tantalum capacitors are generated. Recently, the recovery of tantalum from tantalum capacitors has gained importance especially because of the variable cost and quality associated with the production of tantalum. The Japanese government selected tantalum as one of the 14 priority minerals for recycling and as one of the five most critical minerals for intensive recycling. Therefore, spent tantalum capacitors are an interesting resource for the recovery of tantalum as approximately 40% of the world tantalum production is used towards the fabrication of capacitors. Based on these factors, the development of recycling technologies for spent tantalum capacitors is desirable from the point of view of "urban mines".

Tantalum capacitors consist of a sintered compact matrix comprising sintered tantalum powder used as the electrode, mould resin used as the protective layer for the sintered compact matrix, and a terminal connected to an electrode [1]. To recover tantalum from a tantalum capacitor, the recovery of the sintered compact matrix by removing the stable mould resin layer is important because the tantalum matrix strongly adheres to the mould resin. The mould resin serves as a flame retardant consisting of a halogenated compound. Combustion [2] and solubilisation [3] have been proposed previously for decomposing the mould resin layer. However, these methods have some drawbacks such as high combustion temperature and high reactor pressure requirements and the generation of harmful halogen compounds that necessitates the additional and subsequent use of appropriate treatment.

In our previous studies, we showed that acrylonitrile butadiene styrene (ABS) resin plastics used in computer casing plastics could be decomposed upon pyrolysis with NaOH, and the halogen compounds could be captured in the residue following pyrolysis rather than being discharged in gas phase [4]–[6].

Here, we present a new approach to recover tantalum from tantalum capacitors via pyrolysis using NaOH. At the optimal reaction conditions, tantalum is simply separated, by sieving, from the powdered mould resin obtained upon pyrolysis with NaOH. Furthermore, the halogenated compounds generated upon pyrolysis are captured in sodium hydroxide.

## II. MATERIALS AND METHODS

The tantalum capacitor test materials ( $6.0 \times 3.2 \times 2.5$  mm; Model no. ESVC1V475M) were obtained from NEC/TOKIN Co., Ltd. (Fig. 1). The capacitors comprise tantalum-sintered compact (40%), mould resin (44%), and others (16%). The mould resin consists of molten silica (70%) [7], [8], OCN (o-cresol novolac)-type epoxy resin (15%), phenolic novolac resin (7%), and flame retardants (10%).

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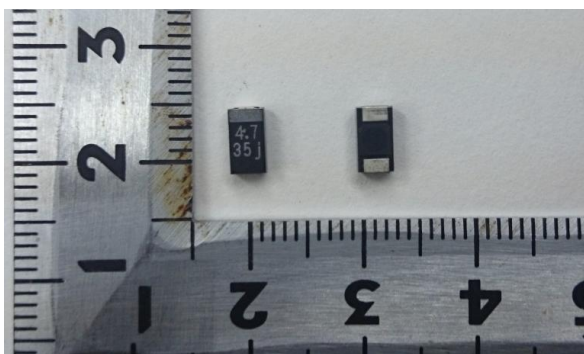


Fig. 1. Tantalum capacitor used in this study.

The experimental apparatus employed in this study is shown in Fig. 2. First, NaOH was introduced into the reactor, and heated in an electric furnace under nitrogen flow (160 mL/min). After heating to the set temperature (350–650 °C), tantalum capacitor (approximately 3 g) was introduced into the reactor, and heated for varying times of 5 min to 24 h. The reaction vessel was then allowed to naturally cool to room temperature. As the capacitor was integrated into the fused salt solid upon pyrolysis, it could be dissolved in distilled water, and subsequent filtration enabled the recovery of the residual substance of the capacitor. The residual percentage contents of the samples were calculated by weight ratio of the residues after the experiment to the original samples to evaluate the decomposition behavior of the samples using NaOH.

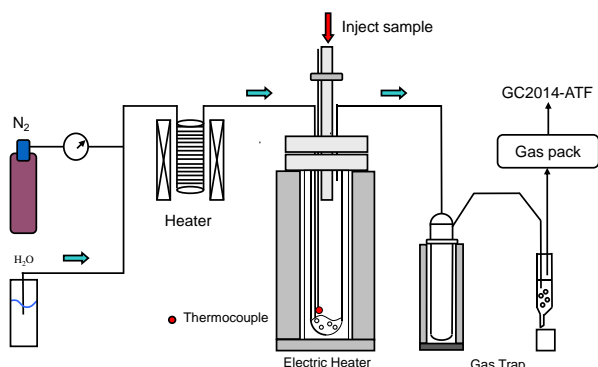


Fig. 2. Experimental apparatus used in this study.

During the experiment, the gas generated during pyrolysis passed through the water-bubbling bottle where the halogen compounds in the gas were captured and analyzed by gas chromatography (GC-2014ATF, SHIMADZU). After the experiment, the halogen contents in the filtrate and the solution in the water-bubbling bottle were analyzed by ion chromatography (DX-120) to estimate the content of halogens trapped in NaOH.

### III. RESULTS AND DISCUSSION

#### A. Effect of Temperature

Fig. 3 shows the residual percentage of the samples after the pyrolysis experiments conducted at varying temperatures. Regardless of the temperature studied, approximately 70 wt.% of the original capacitor remained as residue after the experiment, thus confirming that decomposition of the samples occurred within the temperature range studied

(350–650 °C) using NaOH.

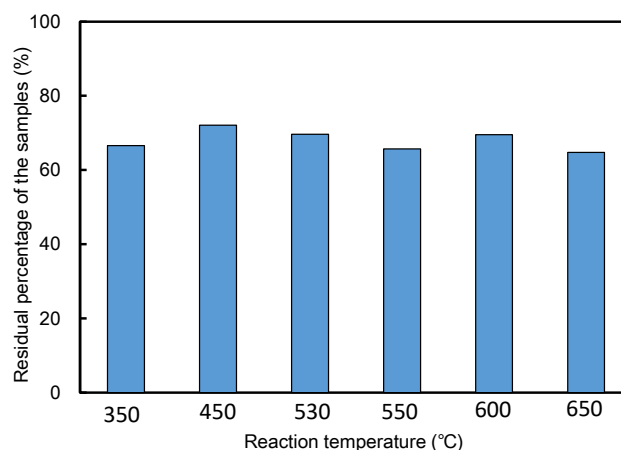


Fig. 3. Residual percentage of the samples after the pyrolysis experiments.

Fig. 4 shows photos of the residues after pyrolysis with NaOH at varying temperatures of 350–650 °C. The mould resin could be completely removed to recover the compact from the capacitor, and collapse of the tantalum-sintered compact was not observed after pyrolysis at 350–550 °C (Fig. 4(a)–(d)). In contrast, collapse of both the mould resin and tantalum compact was observed after pyrolysis at 600 and 650 °C (Fig. 4(e) and (f)). The tantalum-sintered compact could be easily separated from the mould resin when the tantalum-sintered compact was not powdered. These results suggest that tantalum compact can be recovered from the capacitor upon decomposition of the mould resin only using NaOH at 350–550 °C.

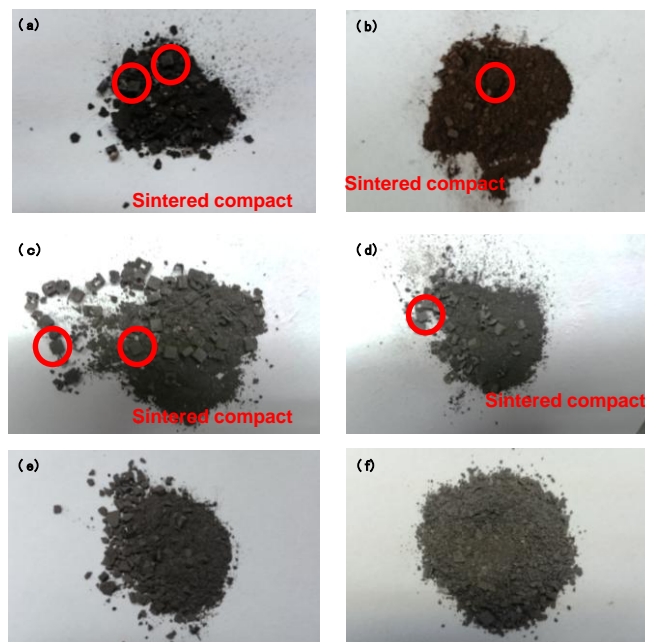


Fig. 4. Photos of the residues after pyrolysis of capacitors with NaOH at (a) 350, (b) 450, (c) 530, (d) 550, (e) 600 and (f) 650 °C. Red circles indicate the tantalum sintered compact without collapse.

Fig. 5 shows the amount of halogen gases generated at various temperatures during the experiment. Halogen contents of F, Cl, and Br were only detected in the residues and not in the gas phase. This result implied that the halogen compounds in the capacitor were captured in NaOH and were not discharged into the gas phase. At pyrolysis temperatures of 350–650 °C, the amounts of F and Br in the residue were

roughly 6 and 24 mg, respectively. Cl in the residue was detected upon pyrolysis at the higher pyrolysis temperatures of 600 and 650 °C.

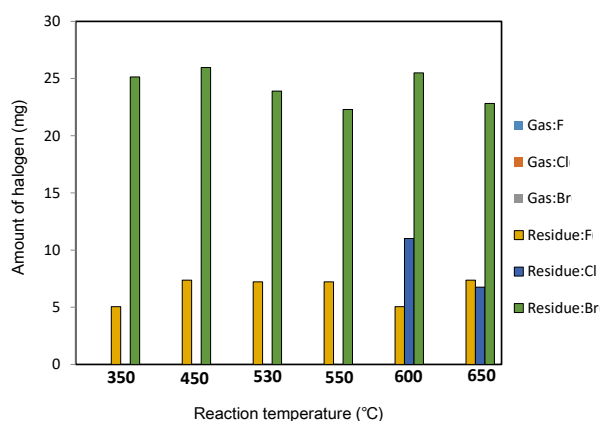


Fig. 5. Amount of halogen generated during the pyrolysis experiments at various temperatures.

Fig. 6 shows the amount of dissolved content in the filtrate from the residues after pyrolysis at various temperatures. As observed, SiO<sub>2</sub> could be extracted from the mould resin at all temperatures studied. In addition, small amounts of metals, Mn, Ni, Ag, Fe, and Cu, were detected. This observation implied that the metal parts in the capacitor did not dissolve upon pyrolysis with NaOH. Furthermore, the amounts of dissolved Ta measured after pyrolysis at 600 and 650 °C were larger than those measured at the lower temperatures studied (i.e., ≤550 °C). This result is consistent with the results obtained relating to the collapse of the tantalum compacts, as shown in Fig. 4.

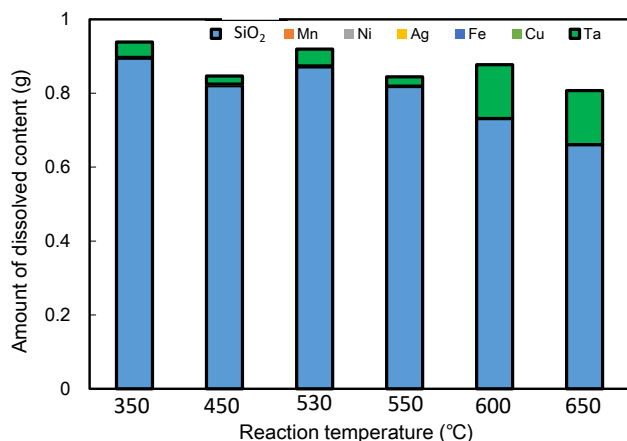


Fig. 6. Amount of dissolved content in the filtrate after treatment of the residues.

Based on the above results, the mould resin could effectively decompose upon pyrolysis with NaOH at 350–650 °C, while halogen gases were captured by NaOH. In contrast, the tantalum components decomposed at the higher temperatures studied (600 and 650 °C). After pyrolysis, the filtrates from the residues comprised high amounts of silica originating from the mould resin and small amounts of metals such as Mn, Ni, Ag, Fe, and Cu. Ta was also originally detected in small amounts, however, increased with increasing pyrolysis temperatures at 600 and 650 °C. Therefore, the spent capacitor was successfully pyrolysed at 350–550 °C with NaOH for the recovery of tantalum-sintered compact from the capacitor.

## B. Effect of Reaction Time

Fig. 7 shows the residual percentage of the samples after the experiments conducted at varying reaction times. As observed, with increasing reaction times, approximately 80 wt.% of the original capacitor remained as residue after pyrolysis for 5 min. The residual mass percentage gradually decreased to 70 wt.% with increasing reaction times.

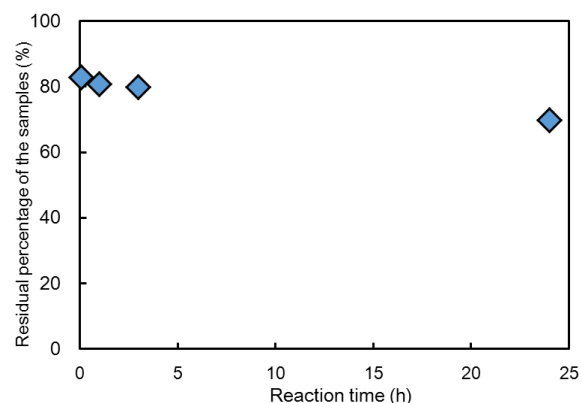


Fig. 7. Residual percentage of the samples after the pyrolysis experiments as a function of heating time at 530 °C.

Fig. 8 shows photos of the residues after pyrolysis for various reaction times. Sintered compacts were observed in all residues. The black powder in the residues was finer following pyrolysis with increasing reaction times.

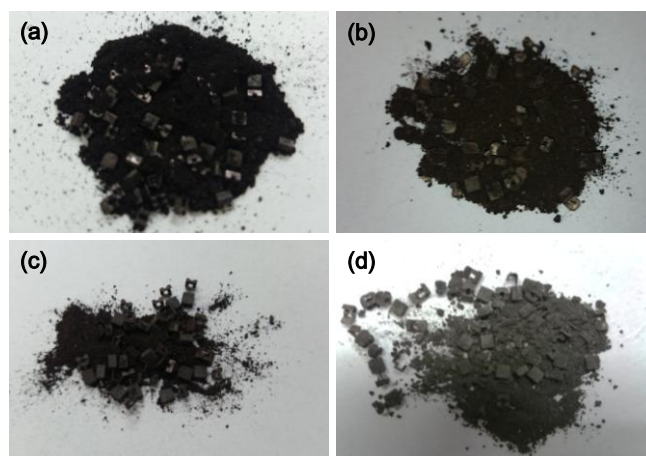


Fig. 8. Photos of the residues after pyrolysis of tantalum capacitor at 530 °C for (a) 5 min, (b) 1, (c) 3 and (d) 24 h.

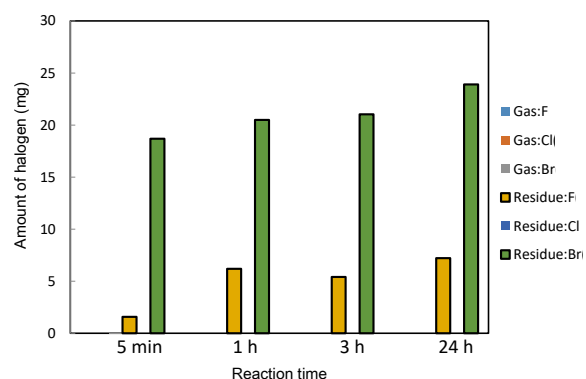


Fig. 9. Amount of halogen generated during the pyrolysis experiments.

Fig. 9 shows the amount of halogen gases generated during the experiments conducted for various reaction times. As observed, with increasing reaction times, the Br content

gradually increased to 25 mg. The F content increased to 5 mg with increasing pyrolysis times to 1 h, and remained constant thereafter.

Fig. 10 shows the amount of dissolved content in the filtrate from the residues obtained during the experiments. With increasing reaction times, the amount of dissolved  $\text{SiO}_2$  gradually increased. In contrast, the amount of dissolved Ta obtained at reaction times of less than 1 h was small, but rapidly increased with increasing reaction times thereafter. Additionally, as noted, the metal contents of Mn, Ni, Ag, Fe, and Cu were low.

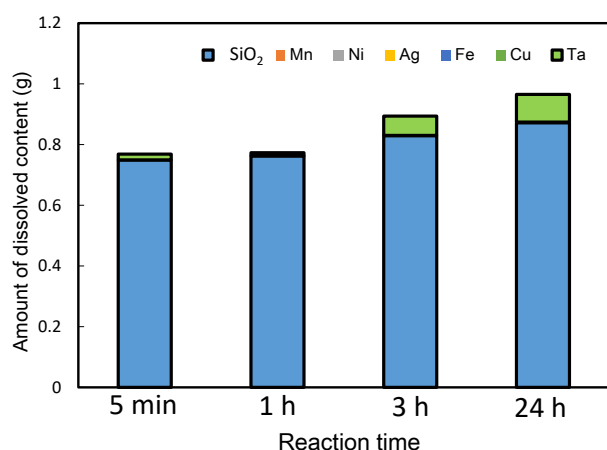


Fig. 10. Amount of dissolved contents in the filtrate after treatment of the residues during the pyrolysis experiments.

Fig. 11 shows the amounts of gas produced from the samples during the experiments. The gases,  $\text{H}_2$ ,  $\text{CH}_4$ , and others (mostly hydrocarbon gases), were produced at the early stages of the reaction (0–20 min), and the amount of these gases gradually decreased to zero with increasing reaction times to 60 min.

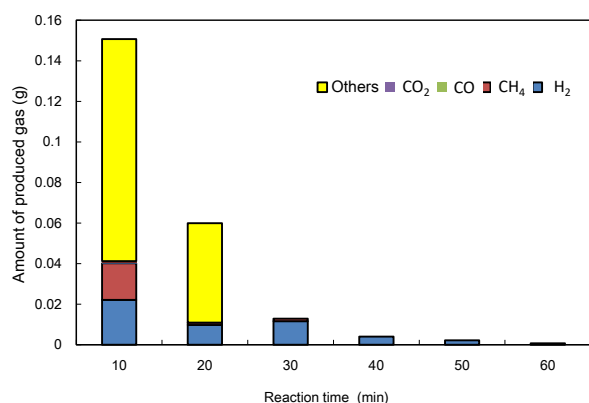


Fig. 11. Amount of gas produced from the samples during the pyrolysis experiments.

Based on these results, at a pyrolysis temperature of  $530^\circ\text{C}$ , most of the mould resin rapidly decomposed within 1 h of reaction, and Ta dissolved in the filtrate after 1 h of reaction.

Fig. 12 shows a photo of the residue on the sieve after pyrolysis with NaOH at  $530^\circ\text{C}$  for 5 min. As observed, the mould resin could be removed completely to recover the compact from the capacitor without collapse of the tantalum-sintered compact.

The following mechanism, as depicted in Fig. 13, is proposed for the decomposition of the mould resin to recover

the tantalum-sintered compact from spent capacitors. The tantalum-sintered compact is covered with the mould resin containing fused silica. Upon heating of the spent capacitor with NaOH in the reactor, first, the organic resin decomposes and gassifies with NaOH, and the halogen compounds generated from the resin are captured in NaOH as sodium soluble salts such as NaBr. Secondly, NaOH contacts with the fused silica particles in the mould resin owing to the decomposition of the organic resin and reacts with the fused silica particles to form sodium silicates. The solid obtained after reaction contains the compact, residual organic resin, soluble salts, residual NaOH, sodium silicates, and sodium halogenated compounds. By adding the solid to distilled water, the soluble salts dissolve into the solution, and the mould resin layer collapses to enable recovery of the tantalum-sintered compact.

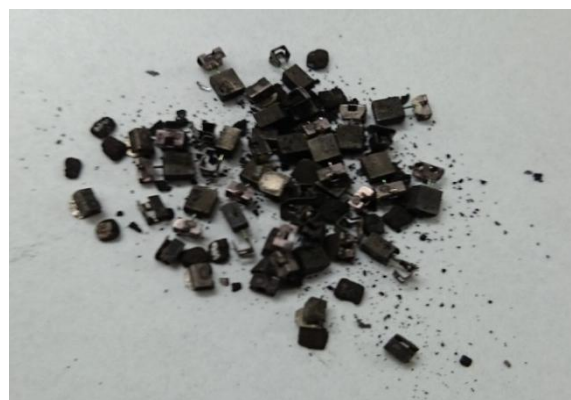


Fig. 12. Photo of the residue on the sieve after pyrolysis of tantalum capacitor with NaOH at  $530^\circ\text{C}$  for 5 min.

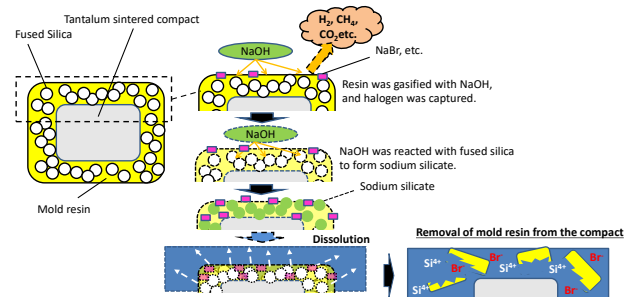


Fig. 13. Proposed reaction scheme for the decomposition of mould resin to recover the tantalum-based compact.

#### IV. CONCLUSION

Herein, the recovery of tantalum-sintered compact in a tantalum capacitor was examined by decomposing the mould resin protective layer using NaOH. The results showed that the mould resin could be decomposed by pyrolysis with NaOH at  $350$ – $650^\circ\text{C}$ . The compact could be recovered by pyrolysis at  $350$ – $550^\circ\text{C}$  following sieving. In contrast, the compact could not be recovered from the capacitor by pyrolysis at higher temperatures of  $600^\circ\text{C}$  and above because both the mould resin and tantalum-sintered compact decomposed as a mixed combined powder that could not be separated. The release of halogen gasses generated upon pyrolysis was inhibited by trapping in NaOH in the reactor. A large amount of  $\text{SiO}_2$  dissolved in the filtrate from the residue after pyrolysis at  $350$ – $650^\circ\text{C}$ . Ta dissolved at pyrolysis



temperatures of 600 and 650 °C. The decomposition of the mould resin occurred rapidly upon pyrolysis at 530 °C. An associated reaction time of 1 h was sufficient to decompose most the mould resin. Thus, the present findings suggest that the protective mould resin layer in tantalum capacitors can be rapidly decomposed by pyrolysis with NaOH at temperatures of less than 550 °C for the recovery of tantalum-sintered compact from tantalum capacitors. Thus, recovery of the tantalum components from the capacitors was successful upon reaction with NaOH at 530 °C for 5 min owing to the effective decomposition and removal of the mould resin from the capacitor. Furthermore, most of the halogen gases generated from the decomposition of the mould resin could be trapped in NaOH, thereby inhibiting exhaustion of halogen gases. These results indicate that the recovery of tantalum from spent capacitors using NaOH is a feasible approach to recycle rare metals in electric equipments. In future work, we will examine the optimum amount of NaOH to continuously decompose the mould resin to recover the tantalum, and develop the effective process to recovery of tantalum from spent capacitor.

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